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A NUMERICAL SIMULATIONS OF ADSORPTION ONTO A CRYSTALLINE SURFACE

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A particular model for the adsorption of a dense fluid onto a crystalline surface has been studied (L. Blum and D.A. Huckaby, J . Chem. Phys 94, 6887 (1991). The fluid is arbitrary and the crystalline surface is modelled by a hard wall decorated with a triangular lattice of sticky sites. This model can be mapped on a lattice gas model with interaction potentials related to the particle distribution functions of the smooth (undecorated) wall problem. Approximate adsorption isotherms in the θ-p plane (fraction of occupied sites vs. bulk density) have also been drawn. However, the effect that the three particle distribution function has on the critical point has also been estimated (D.A. Huckaby and L. Blum, submitted) and it is quite important. Here we have performed Monte Carlo simulations of a model system inspired on this work. It is a 2D systems interacting via a hard sphere plus a triangular well potential and immersed in an external field described by a triangular lattice of sticky sites. We have studied its phase diagram paying some attention also to its behavior in the limit of infinitesimally small sticky adhesion.

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A Numerical Simulation of Adsorption onto a Crystalline Surface

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The sticky site model (SSM) has been recently introduced as a simplified but not too unrealistic model of a structured solid-liquid interface [1]. Here we focus our attention on the adsorbed layer onto a surface that is modelled as a smooth plane surface with sticky points on it. These sticky points form a crystalline lattice representing the adsorption sites and the adsorbed layer feels them as an external potential. This potential u(r) can be represented by its Boltzmann factor

$$exp(-\beta u(r)) = 1 + \sum_{n_1,n_2} \lambda \delta(\mathbf{r} - n_1\mathbf{a}_1 - n_2\mathbf{a}_2) \qquad (1)$$

Here $\mathbf{a}_1$,$\mathbf{a}_2$ describe the lattice, the stickiness parameter λ represents the fugacity of an adsorbed atom and $\beta = 1/kT$.

We have performed MC simulations on a system of 196 particles that interact between themselves with the hard sphere-triangular well potential

$$v(r) = \begin{cases} \infty & r \leq 1 \\ V_1 \frac{r-1}{r_0-1} & 1 < r \leq r_0 \\ 0 & r > r_0 \end{cases}$$

the sticky sites form a triangular lattice of constant $a = r_0$ and are modelled by the potential

$$u(r) = \begin{cases} U_s & r \leq \delta \\ 0 & r > \delta \end{cases}$$

with $r_0 = 1.30$, $\delta = 0.15$. There also are 196 sticky sites, the density is $\eta = \pi N/(4V) = .53$ (close packing is $\eta = .9$) and the parameters that vary are T, V_s and U_s. Several data sets were considered and the runs' length was typically between 20 and 30 10^6 MC steps. In Fig. 1a,b,c,d, we show results for $U_s = V_s = -50$, $T = 15, 25, 40$ and in fig. 1e,f we plot adsorption isotherms as a function of u and adsorption as a function of T with U_s labelling the curves; $V_s = -50$ always. It is seen that the system undergoes a first order phase transition liquid-solid, that the solid commensurates with the lattice of sticky sites and that the uprising in adsorption coincides with $g_2(r)$ developing shoulders corresponding to the triangular lattice peaks.

References

[1] L. Blum, Adv. Chem. Phys. Vol LXXVIII, edited by I. Prigogine and S.A. Rice, John Wiley and Sons, N. York (1990).

Figure Captions

Figure 1. a) Stuck particles probability distribution function for $U_s = V_t = -50$, T=15,25,40 (solid, dot and dashed lines); b) pair distribution function for T=15 and triangular lattice peak positions (solid and dashed); c) idem as b) with T=25; d) idem as b) with T=40; e) adsorption isotherm as a function of U_s for T=15,25,40; f) adsorption as a function of T for U_s= -70,-50,-30.